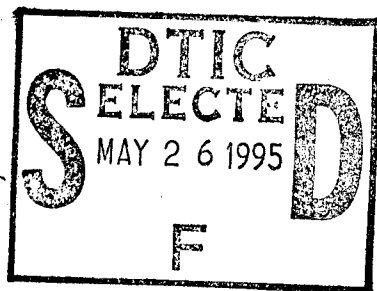


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UNITED STATES ATOMIC ENERGY COMMISSION

TOTAL NEUTRON CROSS SECTIONS OF COMPOUNDS  
WITH DIFFERENT CRYSTALLINE STRUCTURES



by  
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By Lester Winsberg, David Meneghetti, and S. S. Sidhu

The total neutron cross sections of polycrystalline compounds, such as close-packed hexagonal ZnO, body-centered cubic TlBr, and face-centered cubic CaO and TiC were determined with the Argonne neutron velocity selector and neutron crystal spectrometer in the energy region of 0.001 to 1.0 electron volt. From the size of the cross section peaks which are due to coherent scattering of neutrons the following scattering amplitudes were determined: Ca,  $+0.46 \times 10^{-12}$  cm; Ti,  $-0.25 \times 10^{-12}$  cm; Tl,  $+0.75 \times 10^{-12}$  cm. The previously reported value of  $+0.58 \times 10^{-12}$  cm for Zn was confirmed. The free atom scattering cross section of Ca is 2.5 barns.

Interference effects are observed when photons or particles of appropriate wave length impinge on crystalline matter. For diffraction to occur the wave length of the impinging radiation must be less than twice the largest interplanar distance in the crystal but not smaller by too large an order of magnitude. The intensity of the scattered beam is usually measured as a function of the scattering angle and the wave length of the impinging radiation. Since the intensity of the transmitted beam is decreased by the amount of scattered and absorbed radiation, diffraction effects may also be observed if transmission measurements are made as a function of the wave length of the incident beam.

## Experimental Procedure and Results

The two devices used for velocity selection of neutrons from the Argonne heavy water pile were the rotating shutter mechanism designed by Brill and Lichtenberger<sup>4</sup> and the crystal spectrometer described by Zinn<sup>5</sup> and Strum<sup>6</sup>. The rotating shutter mechanism employs the time of flight method for determining the energy of neutrons. Its operating range was 0.001 to 0.2 electron volt. The energy range of neutrons obtained by means of the crystal spectrometer was 0.1 to 1.0 electron volt.

The samples were in the form of powders ground to finer than 200 mesh and were contained in aluminum containers with inner end dimensions of  $1\frac{1}{2} \times 4\frac{1}{2}$  inches and lengths varying from 2 to 10 inches, depending on the desired transmissions in the region of 0.25 to 0.5. In the case of samples with high absorption and low scattering of neutrons it was necessary to use a sample having low transmission in order to determine with sufficient accuracy the contribution of coherent scattering to the total cross section of the material.

The transmission T of the sample for neutrons of given velocity was determined from the ratio of the counting rates obtained with and without the sample in the path of the beam corrected for the fast neutron background. From the weight of the sample and the inner end area of the container the number N of formula molecules per unit end area was calculated. The cross section was then determined from

$$\sigma = \frac{1}{N} \ln \frac{1}{T} \quad (1)$$

The theoretical cross section curves due to coherent scattering alone were calculated from the relation<sup>3</sup>:

$$\sigma = \sum_{\substack{n \leq \frac{2}{\lambda} \\ d}} \frac{FM\lambda^2 d}{gV8\pi n} e^{-\omega(n/d)^2} \quad (2)$$

in which the structure factor  $F$  of the lattice made up of diatomic substance was calculated as follows:

$$F = 4\pi \left| A_1 \sum_{u_1 v_1 w_1} \exp [2\pi i(hu_1 + kv_1 + lw_1)] + A_2 \sum_{u_2 v_2 w_2} \exp [2\pi i(hu_2 + kv_2 + lw_2)] \right|^2 \quad (3)$$

where  $A_1$  and  $A_2$  are the scattering amplitudes of atoms of species 1 and 2;  $u$ ,  $v$  and  $w$  the coordinates of the atoms in the unit cell and  $h$   $k$   $l$  the Miller indices. In expression (2)  $M$  is the multiplicity factor (the number of different orientations of the unit cell such that the Bragg condition for a given set of crystal planes is satisfied),  $\lambda$  the wave length of the neutrons,  $V$  the volume of the unit cell,  $d$  the interplanar spacing for a given set of crystal planes,  $n$  the order of reflection and  $g$  the number of molecules per unit cell. The exponential term is a Debye-Waller type correction factor for thermal agitation, in which  $\omega$  is a function of the Debye temperature.<sup>2</sup>

Where the scattering amplitudes were known the coherent scattering cross section as a function of energy was calculated from equations (2) and (3). The contribution due to absorption was calculated from the value of the absorption cross section at 0.025 electron volt<sup>7</sup> on the assumption that the absorption cross section varied inversely proportional to the neutron velocity. The sum of the two calculated cross sections was compared with the experimentally obtained values. Where the scattering amplitude was not known its value was taken to be that which gave the best fit of the resultant curve above and below the position of the first appearance of diffraction effects.

It should be noted that for  $n^{\text{th}}$  order diffraction from a given set of parallel planes the maximum cross section occurs at the wave length  $\lambda = 2d/n$ . The energy values corresponding to these wave lengths are marked on all the figures given below. The coherent scattering cross section for neutrons of wave length longer than  $2d/n$  is zero for the given value of  $n$  and  $d$ .

#### A. CaO

An 8 inch long container was filled with 476.8 grams of chemically pure CaO which had been dried for several days at 950°C. The sample was kept in a desiccator at all times except during an actual cross section measurement. These precautions were necessary to avoid absorption of water.

The structure of calcium oxide is face-centered cubic. Fermi and Marshall<sup>7</sup> give the scattering amplitudes of Ca and O as 0.79 and 0.61 respectively in units of  $10^{-12}$  cm. The signs of the scattering amplitudes are both positive, i.e., the change in the phase of the neutron wave on scattering by Ca is the same as for O. As given in Table 1, the structure factors for diffractions involving all odd indices are proportional to the factor (Ca-O) where the chemical symbols represent the scattering amplitudes. For all even indices the factors are proportional to (Ca + O). This is confirmed by Figure 1. The first two peaks can be unambiguously assigned to diffraction involving even indices (200) and (220). Furthermore, the (111) peak is either very weak or completely absent. The positions of the other peaks are in accord with the assigned signs of the scattering amplitudes, although the agreement in these cases is not as definite. Because of the limited resolution of the instrument, the cross section peaks obtained experimentally occur at slightly higher energies than the calculated values.

The calculated cross section curve, based on the data of Fermi and Marshall<sup>8</sup> and a value of 570°K for the Debye temperature determined from the heat capacity data, is larger than the experimental curve obtained here by a factor of almost 2. The best fit of the experimental and calculated curves was for a value of  $0.46 \pm .05$  for the scattering amplitude of Ca based on the value of 0.61 for O. The free atom scattering cross section of Ca can be calculated by the formula  $\sigma = 4\pi A^2 \mu^2$  where  $A$  is the value of the scattering amplitude and  $\mu$  is the reduced mass of a neutron and a free Ca atom. This formula

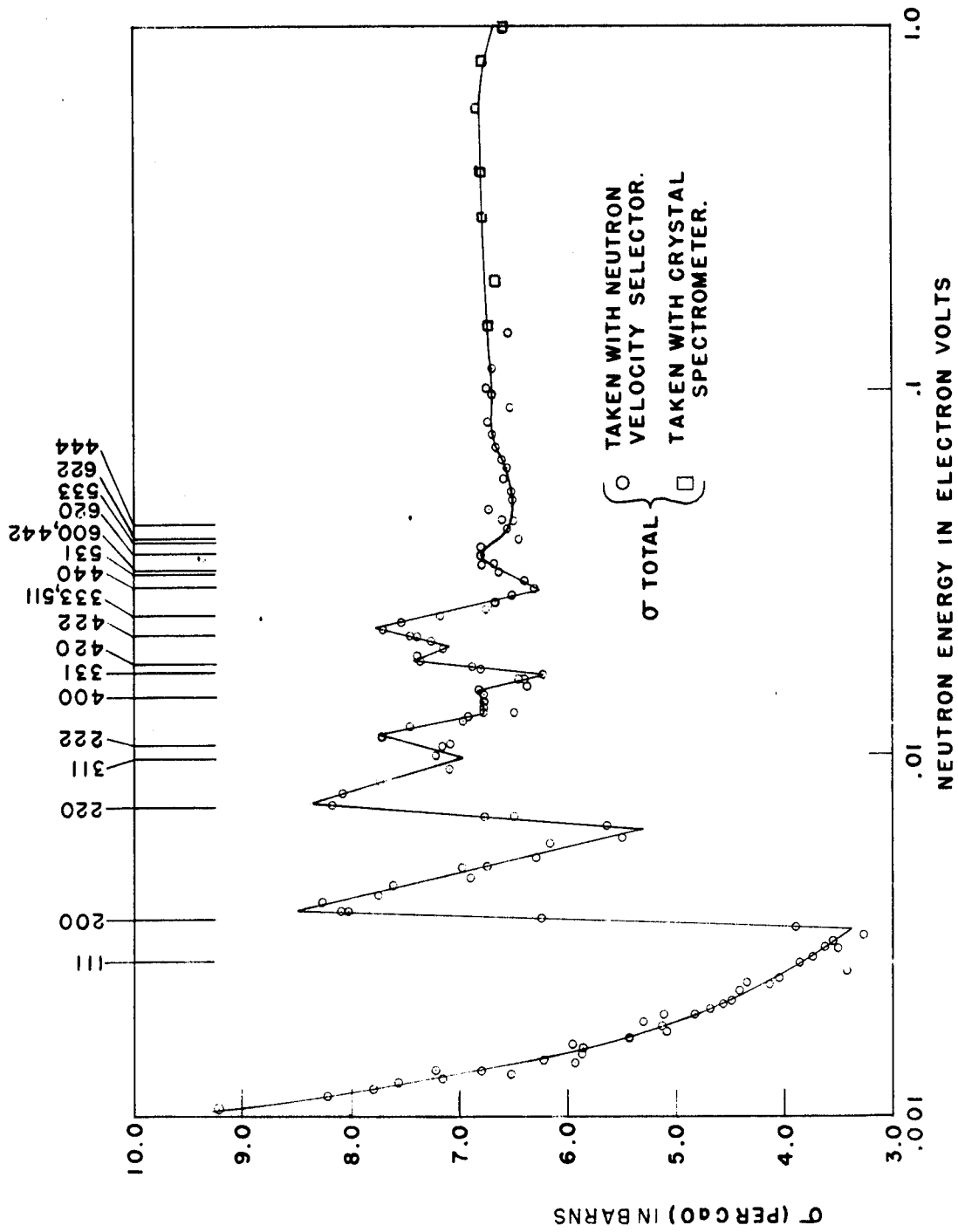


Figure 1. Neutron cross section of CaO versus neutron energy.

is strictly valid only for mono-isotopic elements but is assumed accurate enough here within the uncertainty in the scattering amplitude, since isotopic abundance of  $\text{Ca}^{40}$  is 97%, the remainder being divided among 5 isotopes. The free atom scattering cross section based on the value of 4.1 barns for 0 was also determined from the experimental curve at one electron volt. The value obtained by both the rotating shutter method and the crystal spectrometer was  $2.5 \pm 0.3$  barns. It is much less than any value previously reported.

#### B. TiC

A 2 inch long container was filled with 378.2 grams of TiC. Since the compound has a low avidity for water further drying was unnecessary.

Like CaO, TiC crystallizes in a face-centered cubic structure. While the scattering amplitude of C is given as  $+0.67^8$  neither the sign nor the magnitude of the scattering amplitude of Ti has been known.

Whereas in the case of CaO the cross section values for diffractions involving even indices was large and those involving odd indices very small, the situation is reversed in the case of TiC. As seen in Figure 2 the intense peaks can be unambiguously assigned to diffractions from the (111) and (311) planes. Possible peaks corresponding to the (200) and (220) planes are relatively weak. The change in the phase of the neutron on scattering by Ti is, therefore, different by the angle  $\pi$  from that for C, i.e., the sign of its scattering amplitude is negative. The large continuous rise of the curve with decreasing energy is due primarily to the high  $1/v$  absorption cross section of titanium. The scattering amplitude was calculated from the curve to be  $-0.25 \pm 0.03$ . The Debye temperature was not known. Calculations were, therefore, made by assuming it to be  $500^\circ\text{K}$ ,  $1000^\circ\text{K}$ , and  $1500^\circ\text{K}$ . The lowest value of the exponential term in equation (2) for the (111) planes was 0.96 for a Debye temperature of  $500^\circ\text{K}$ . Because the term decreases in magnitude for larger indices, the value of the scattering amplitude was calculated primarily from the (111) peak and is, therefore, relatively reliable. The structure factors for various crystalline planes of TiC, based on the above value of the scattering amplitude of Ti, and the multiplicity factors are given in Table 1.

#### C. TlBr

A container similar to that used for TiC was filled with 887.5 g of TlBr which had been dried for 3 days at  $400^\circ\text{C}$ . The scattering amplitude of Br is given as  $+0.56^8$ , and that of Tl is determined here.

The structure of TlBr is of the CsCl type, in which the cross section values depend strongly on whether the sum of the Miller indices is even or odd. For scattering amplitudes with like sign, large cross section peaks will occur at positions corresponding to indices of even sum. On the other hand if the Tl and Br atoms scatter neutrons out of phase the peaks corresponding to indices of odd sum would be prominent.

As shown in Figure 3 the peaks in the cross section curve occur at positions corresponding to an even sum of Miller indices. Thus, Tl and Br scatter in phase, i.e., the sign of the scattering amplitude of Tl is positive. From analysis of the curve the magnitude of the scattering amplitude was found to be  $0.75 \pm 0.08$ , based on the value of  $+0.56$  for Br.<sup>8</sup> A Debye temperature of  $\sim 500^\circ\text{K}$ , determined from heat capacity data, was used in the calculations. The structure and the multiplicity factors for this compound are also given in Table 1.

#### D. ZnO

A 6 inch long container was filled with 873.7 grams of ZnO, which had been dried for several days at  $900^\circ\text{C}$  and a total cross section curve as a function of energy was obtained as shown in Figure 4. Since this compound crystallized in a close-packed hexagonal structure with the following coordinates of the atoms in the unit cell, Zn: 000,  $1/3$ ,  $2/3$ ,  $1/2$ , and O:  $00\mu$ ,  $1/3$ ,  $2/3$ ,  $(1/2 + \mu)$  where  $\mu = 0.3725$ , its structure factor is given by the expression:

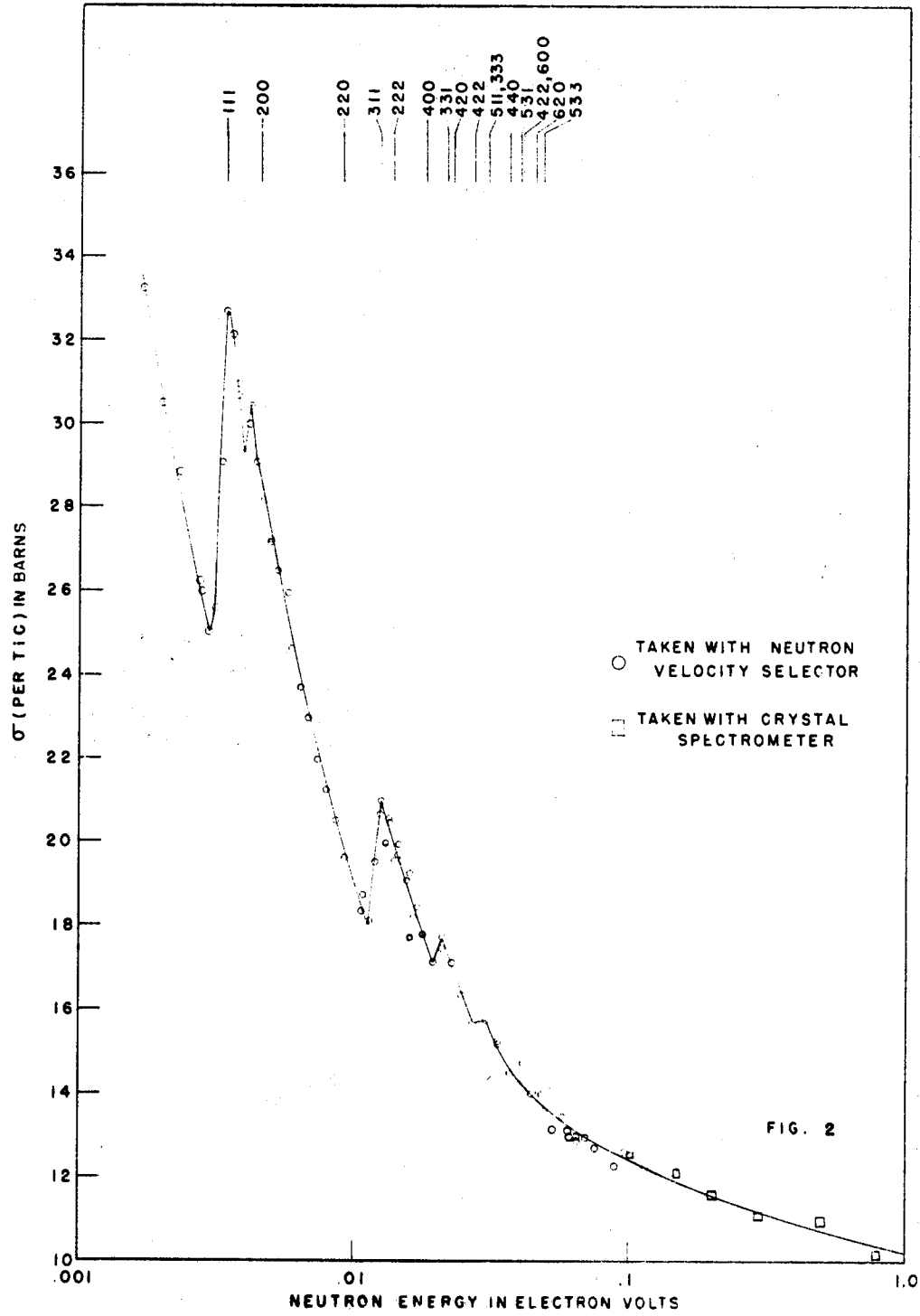


Figure 2. Neutron cross section of TIC versus neutron energy.

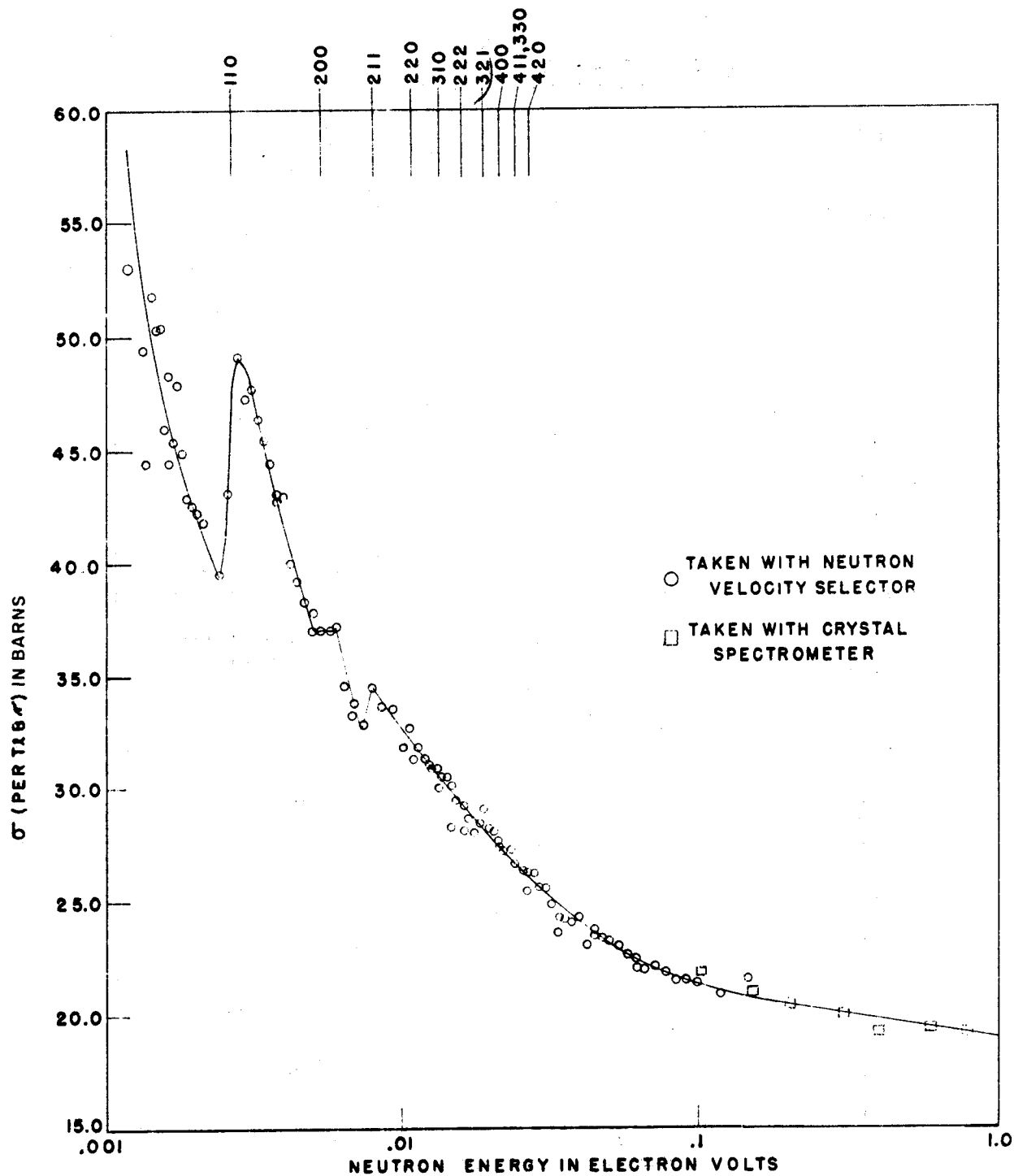


Figure 3. Neutron cross section of  $\text{TiB}_4$  versus neutron energy.

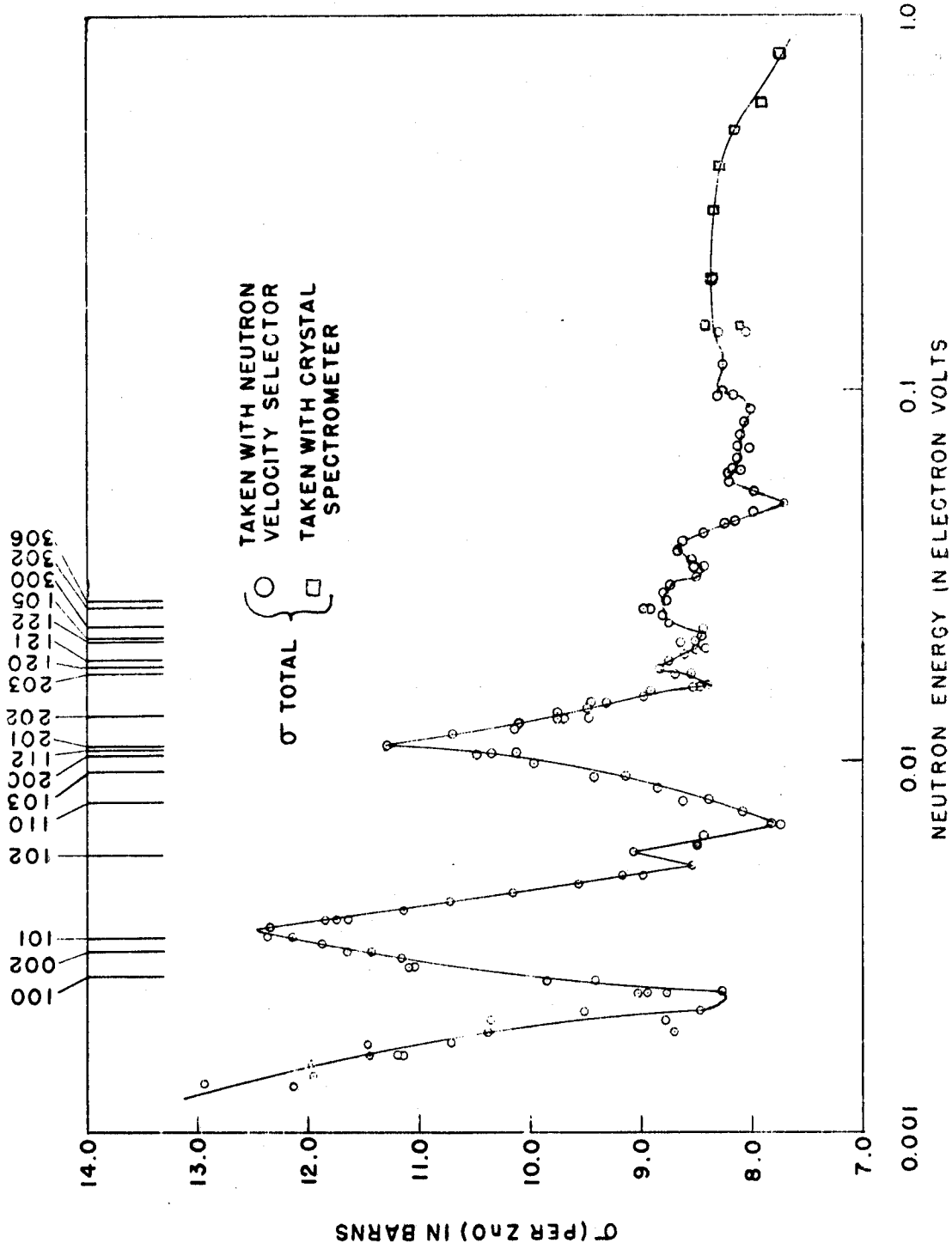


Figure 4. Neutron cross section of ZnO versus neutron energy.



Table 1. Structure factors and multiplicity factors of CaO, TiC, TlBr and ZnO.

Element	Miller indices	M	F/4 $\pi$	FM/4 $\pi$ $\times 10^{-24}$ cm <sup>2</sup>
CaO	111	8		3
	311	24	16(Ca - O) <sup>2</sup>	9
	331	24		9
	—			
	200	6		110
	220	12	16(Ca + O) <sup>2</sup>	220
	222	8		146
	—			
	200	6		17
TiC	111	8		109
	311	24	16(Ti - C) <sup>2</sup>	326
	331	24		326
	—			
	200	6		17
	220	12	16(Ti + C) <sup>2</sup>	34
	222	8		23
	—			
	200	6		10.3
TlBr	100	6		0.2
	111	8	(Tl - Br) <sup>2</sup>	0.3
	210	24		0.9
	—			
	110	12		20.6
	200	6	(Tl + Br) <sup>2</sup>	10.3
	211	24		41.3
	—			
	200	6		8.5
ZnO	002	2	(Zn + O) <sup>2</sup>	5.5
	101	12	4(Zn + O <sup>2</sup> - .070 Zn .O)	7.8
	102	12	3(Zn + O <sup>2</sup> - 1.39 Zn .O)	8.2
	110	6	(Zn + O <sup>2</sup> - .070 Zn .O)	34.0
	103	12	4(Zn + O) <sup>2</sup>	44.4
	200	6	3(Zn <sup>2</sup> + O <sup>2</sup> + 1.49 Zn .O)	8.5
	112	12	(Zn + O) <sup>2</sup>	32.8
	201	12	4(Zn <sup>2</sup> + O <sup>2</sup> - .070 Zn .O)	7.8
	004	2	3(Zn <sup>2</sup> + O <sup>2</sup> - 1.39 Zn .O)	0.02
	—		4(Zn <sup>2</sup> + O <sup>2</sup> - 1.995 Zn .O)	
	—			

Table 2. Scattering amplitudes of Ca, Ti, Tl and Zn.

Element	Scattering amplitude (units of 10 <sup>-12</sup> cm)	Remarks Based on scattering amplitude of:
Ca	+ 0.46 $\pm$ 0.05	O, as + 0.61 $\times$ 10 <sup>-12</sup> cm
Ti	- 0.25 $\pm$ 0.03	C, as + 0.67 $\times$ 10 <sup>-12</sup> cm
Tl	+ 0.75 $\pm$ 0.08	Br, as + 0.56 $\times$ 10 <sup>-12</sup> cm
Zn	+ 0.58	Same as reported previously <sup>8</sup>

$$F = 8\pi \left[ 1 + \cos 2\pi(h/3 + 2k/3 + l/2) \right] \left[ Zn^2 + O^2 + 2 ZnO \cos 2\pi\mu l \right] \quad (4)$$

in which Zn and O represent scattering amplitudes of the corresponding nuclei. When the previously determined values<sup>8</sup> of the scattering amplitudes, +0.58 for Zn and +0.61 for O are substituted in (4) the expression reduces to:

$$F = 17.8 + 10^{-24} \left[ 1 + \cos 2\pi(h/3 + 2k/3 + l/2) \right] \left[ 1 + \cos 0.745 \pi l \right] \quad (5)$$

A cross section curve calculated from the structure factors obtained by means of (5) and the multiplicity factors given in Table 1 gave a good fit with the experimentally determined curve. This confirmed both the magnitudes and the signs of the previously determined scattering amplitudes. Were the sign of Zn opposite from that of O, the last factor in (5) would be  $(1 - \cos 0.745 \pi l)$ .

In an x-ray diffraction pattern of ZnO lines of relatively strong intensities are observed from planes such as (100), (002), (101) (102), (110), (103) (200), (112), (201) etc., whose Miller indices satisfy the following conditions:

$$\begin{aligned} \text{when } l \text{ is odd, } h + 2K &= 3n \pm 1 \\ l \text{ is even, } h + 2K &= 3n, 3n \pm 1 \text{ (i.e., any integer)} \\ \text{where } n &= 0, 1, 2, 3 \dots \end{aligned}$$

Because of poor resolution of the rotating shutter device the peaks in the total neutron cross section curve are actually caused by several planes which give strong reflections.

#### Discussion of Results

As seen from the curves presented here most of the diffraction effects are observed in the energy region 0.001 to 0.2 electron volt, which is covered by the rotating shutter device. While the resolution of the device is not comparable to that of the neutron or x-ray crystal spectrometer, enough diffraction peaks characteristic of the crystal system studied are observed that they permit unambiguous determinations of the magnitude and the sign of the scattering amplitudes as summarized in Table 2.

The experimentally determined values of the total cross sections were somewhat higher than the corresponding calculated values for coherent scattering and absorption. The difference is significant and is a proper problem for future investigation.

This method of studying crystalline effects seems to be relatively feasible for those substances that have sufficiently low neutron absorption cross sections. An important application of this method can be made in the determination of the structures of compounds containing hydrogen and deuterium. By means of the usual x-ray diffraction methods the positions of all but the hydrogen and deuterium atoms can usually be determined. This limitation does not exist for neutrons, however, since hydrogen and deuterium have substantial scattering cross sections. If only a limited number of possible arrangements remain for the hydrogen and deuterium atoms after x-ray analysis, the method reported here might supply just the information required for a complete establishment of the structure.

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